

CLAIMS

1. Method for preparing a suspension of a silicic particulate filler, in a silicone material (SM) comprising:

5 > *SM₁*polyaddition:

- at least one type A polyorganosiloxane POS carrying alkenyl crosslinking functional groups *Fa* capable of reacting with the crosslinking functional groups *Fb* (SiH) of at least one B type POS, this A POS being taken alone or as a mixture with at least one nonreactive (E) POS;
- 10 ▪ and at least one B type POS carrying crosslinking functional groups *Fb* (SiH) capable of reacting with the alkenyl crosslinking functional groups *Fa* of the A POS(s);

o and/or *SM₂*polycondensation:

- at least one C type POS carrying hydroxyl crosslinking functional groups *Fc* and/or OR functional groups (R = C₁-C₃₀ alkyl, C₂-C₃₀ alkenyl, aryl, which are optionally substituted (preferably halogenated)) precursor of the functional groups *Fc'*, these crosslinking functional groups *Fc* being capable of reacting with crosslinking functional groups *Fc* of this C POS or of other C POSs, and with crosslinking functional groups of at least one crosslinking agent *D*, this C POS being taken alone or as a

mixture with at least one nonreactive (E) POS;

➤ and/or SM_3 polydehydrogenocondensation:

- at least one C' type POS carrying hydroxyl crosslinking functional groups Fc' and/or OR' functional groups ($R' = C_1-C_{30}$ alkyl, C_2-C_{30} alkenyl, aryl, which are optionally substituted (preferably halogenated)) precursor of the functional groups Fc' , these crosslinking functional groups Fc' being capable of reacting with other crosslinking functional groups Fb' (SiH) of at least one B' type POS, this C' POS being taken alone or as a mixture with at least one nonreactive (E) POS;
- and at least one B' type POS carrying crosslinking functional groups Fb' (SiH) capable of reacting with the crosslinking functional groups Fb' OH or OR' of the C' POS(s);

➤ and/or SM_4 :

- or at least one nonreactive (E) POS;
- this suspension being capable of being used in particular for producing compositions which can be crosslinked by polyaddition and/or by polycondensation and/or by dehydrogenocondensation or antifoam silicone compositions;
- this method being of the type in which an aqueous suspension of silicic particulate filler is made hydrophobic by treating with at least one halogenated

reagent, this treatment comprising a transfer of the silica made hydrophobic into a nonaqueous phase and at least one step for at least partial removal of water;

5 • the compatibilizing agent (CA) being:

- ~ CA I (Route I): either selected from silazanes, taken alone or as a mixture with each other, preferably from disilazanes, hexamethyldisilazane (HMDZ) combined or
10 otherwise with divinyltetramethyldisilazane being particularly preferred;
- ~ CA II (Route II): or selected from R^c -substituted halogenosilanes with R^c = hydrogeno, C_1 - C_{30} alkyl, C_2 - C_{30} alkenyl,
15 aryl, and R^c being optionally substituted (preferably halogenated), preferably from R^c -substituted chlorosilanes and the mixtures thereof;

the said method being characterized:

20 1. in that:

➤ according to route I:

Ia)-- the particulate filler is selected from the group of precipitated silicas,

Ib)-- the compatibilizing agent (CA.I) is

25 added in one or more fractions which are quantitatively and/or qualitatively identical to or different from each other, to the

preparation medium,

Ic)-- the mixing of all or part of the SM, of the filler, of water, and of the CA or CAs is optionally partly carried out in the hot

5 state and in such a manner that the quantity of water is such that the weight ratio $r = (\text{water}/\text{water} + \text{silica}) \times 100$ is defined as follows: $40 \leq r \leq 99$, preferably $60 \leq r \leq 90$,

10 Id)-- optionally at least some of the water released and of the by-products of the reaction of CA.I with SM and with the filler are drawn off,

Ie)-- the volatile species are optionally removed, preferably in the hot state under a
15 gaseous stream or under vacuum,

If)-- and cooled if necessary,

➤ according to route II:

IIa)-- an aqueous silica suspension is prepared or used which comprises:

- 20
- silica,
 - water which is optionally acidified,
 - at least one hydrogen bond stabilizer,

IIb)-- optionally, part of the silicone material SM is incorporated into the aqueous
25 silica suspension obtained at the end of step IIa),

IIc)-- hydrophobic units formed by

$\equiv\text{Si}-(\text{R}^c)_{1 \text{ to } 3}$ with R^c = hydrogeno, $\text{C}_1\text{-C}_{30}$ alkyl, $\text{C}_2\text{-C}_{30}$ alkenyl, aryl, these groups R^c being optionally substituted (preferably halogenated), are grafted onto the silica by exposing this silica to halosilane type CA II acting as precursors of these units and by allowing the reaction to proceed, preferably while stirring the whole, optionally in the hot state,

IIId)-- the procedure is carried out such that the transfer of the silica grafted by hydrophobic units, from the aqueous phase to the nonaqueous phase, is carried out,

IIe)-- optionally, at least part of the aqueous phase and of the reaction by-products is drawn off,

IIIf)-- the medium is cooled if necessary,

IIIg)-- optionally, the residual acidity of the nonaqueous phase is washed off,

IIH)-- the totality or the remainder of the silicone material SM is mixed with the filler which is now hydrophobic,

IIi)-- the residual water is evaporated off,

IIj)-- and an oil is recovered which consists of a hydrophobic particulate filler suspension in a crosslinkable silicone material, preferably without ever passing via

a dried hydrophobic silica,
the routes I and II leading to an oil (or slurry)
consisting of a suspension of hydrophobic
particulate filler in a crosslinkable silicone
material;

2. and in that at least one other compatibilizing
agent (CA III) is used which is chosen from the
group comprising:

- (i) POSSs carrying in and/or at the ends of
their chains compatibilizing functional
groups OR^{IIIi} in which R^{IIIi} independently
corresponds to hydrogen or to a radical
corresponding to the same definition as
given above for R^c ;
- (ii) siloxane resins;
- (iii) silanes;
- (iv) and mixtures thereof;

excluding:

- di- or monofunctional low-molecular-weight
(advantageously less than 1 000 g/mol)
siloxanes with hydroxyl ends;
- amines, such as, for example alkylamines,
(such as diethylamine) and/or silylamines;
- and surfactants and more particularly
cationic surfactants.

2. Method according to Claim 1, characterized
in that the compatibilizing agent (CA III) is chosen

from the group comprising:

- (i) POSSs carrying in and/or at the ends of their chains compatibilizing functional groups OR^{IIIi} in which R^{IIIi} independently corresponds to hydrogen or to a radical corresponding to the same definition as given above for R^c ;
- (ii) siloxane resins;
- (iii) silanes;
- (iv) and mixtures thereof;

provided that C1 according to which if CA = CA I and if CA III comprises at least one α,ω -dihydroxylated POS (i), then the latter is combined with at least one element of the subgroups (ii) to (iii); and without excluding:

- di- or monofunctional low-molecular-weight (advantageously less than 1 000 g/mol) siloxanes with hydroxyl ends;
- amines, such as, for example alkylamines, (such as diethylamine) and/or silylamines;
- and surfactants and more particularly cationic surfactants.

3. Method according to Claim 1,

characterized in that the compatibilizing agent (CA III) is chosen from the group comprising:

- (i) POSSs carrying in and/or at the ends of

their chains compatibilizing functional groups OR^{IIIi} in which R^{IIIi} independently corresponds to hydrogen or to a radical corresponding to the same definition as given above for R^c ;

- (ii) siloxane resins;
- (iii) silanes;
- (iv) and mixtures thereof;

provided that C2 according to which if CA = CA I, then CA I is different from any compatibilizing agent selected from silazanes, taken on their own or as a mixture with each other, in particular disilazanes such as hexamethyldisilazane (HMDZ) combined or otherwise with divinyltetramethyldi-silazane:

and without excluding:

- di- or monofunctional low-molecular-weight (advantageously less than 1 000 g/mol) siloxanes with hydroxyl ends;
- amines, such as, for example alkylamines, (such as diethylamine) and/or silylamines;
- and surfactants and more particularly cationic surfactants.

4. Method according to Claim 1, characterized in that the compatibilizing agent (CA III) is chosen from the group comprising:

- (i) POSS carrying in and/or at the ends of

their chains compatibilizing functional groups OR^{III} in which R^{III} independently corresponds to hydrogen or to a radical corresponding to the same definition as given above for R^c ;

- (ii) siloxane resins;
- (iii) silanes;
- (iv) and mixtures thereof;

and in that this compatibilizing agent (CA III) is combined with at least one condensation catalyst preferably selected from:

- o strong bases, and still more preferably from the subgroup comprising: KOH, LiOH, NaOH and mixtures thereof;
- o metal salts, and still more preferably from the subgroup comprising: tin salts, titanium salts and mixtures thereof;
- o salts of triflic acid;
- o and mixtures thereof;

and without excluding:

- di- or monofunctional low-molecular-weight (advantageously less than 1 000 g/mol) siloxanes with hydroxyl ends;
- amines, such as, for example alkylamines, (such as diethylamine) and/or silylamines;
- and surfactants and more particularly

cationic surfactants.

5. Method according to any one of Claims 1 to 4, characterized in that the compatibilizing agent CA III is incorporated after CA I or CA II, preferably after drawing off all or part of the aqueous phase, provided that the said drawing off takes place.

6. Method according to any one of Claims 1 to 5, characterized in that CA III is added in an amount of 0.5 to 40% by weight, preferably 0.5 to 30% by weight relative to the quantity of silicic particulate filler used in the suspension.

7. Method according to any one of Claims 1 to 6, characterized in that there are chosen:

- one or more precipitated silicas, preferably existing mainly in slurry form and whose BET specific surface area is between 50 and 400 m²/g,
- and mixing conditions such that the dynamic viscosity at 25°C of the suspension is less than or equal to 300 Pa.s, preferably less than or equal to 150 Pa.s.

8. Method according to Claim 1, characterized in that in route II, at least one precursor of silicone resin MQ, preferably a silicate, and still more preferably a sodium silicate, is used in step IIa).

9. Method according to Claim 1,

characterized in that in route II, the hydrogen bond stabilizer/initiator is chosen from organic solvents, preferably from the group comprising alcohols, ketones, amides, alkanes and mixtures thereof.

5 10. Method according to any one of Claims 1 to 6, characterized in that in route II, the acidification of the aqueous suspension (aqueous phase) is carried out using an acid, preferably an inorganic acid, and still more preferably an acid is chosen from
10 the group comprising: HCl, H₂SO₄, H₃PO₄ and mixtures thereof.

 11. Method according to any one of Claims 1 to 7, characterized in that, in route II, the silicone material SM comprises at least one oligoorganosiloxane,
15 preferably a diorganosiloxane, and still more preferably hexamethyldisiloxane (M₂).

 12. Method according to any one of Claims 1 to 8, characterized in that the silica used is precipitated silica(s).

20 13. Method according to any one of Claims 1 to 9, characterized in that a polyaddition SM SM₁ is used which contains:

- at least one reactive silicone oil A POS whose crosslinking functional groups Fa are alkenyl -
25 preferably vinyl - functional groups,

these A POSs:

- comprising at least two Si-Fa groups

per molecule, preferably each situated at one end of the chain,

- and having a dynamic viscosity at 25°C of less than or equal to 250 Pa.s, preferably 100 Pa.s and still more preferably 10 Pa.s,

this A POS being intended to react with the B POS,

- at least one reactive silicone oil B POS, whose crosslinking functional groups Fb are hydrogen functional groups, this B POS comprising at least two groups Si-H per molecule (preferably at least three when the A POS comprises only two Si-Vi groups per molecule), these Si-H groups being advantageously situated in the chain,
- and/or at least one nonreactive E POS;

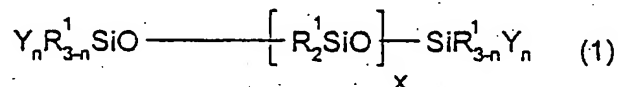
and in that the following are incorporated:

- o a catalytic system comprising a polyaddition metal catalyst (preferably of platinum nature) and optionally an inhibitor;
- o optionally one or more semireinforcing, nonreinforcing or bulking fillers;
- o optionally water;
- o optionally one or more additives chosen from pigments, plasticizers, other rheology modifiers, stabilizers and/or adhesion

promoters.

14. Method according to any one of Claims 1 to 10, characterized in that a polycondensation SM SM_2 is used which contains:

- at least one reactive silicone oil C POS whose crosslinking functional groups F_c react by polycondensation, these C POSSs corresponding to the following formula (1):



in which:

- * R^1 represents monovalent hydrocarbon radicals which are identical or different, and Y represents hydrolysable or condensable groups OR^{11} with R^{11} corresponding to the same definition as that given above for R^c ,
- * n is chosen from 1, 2 and 3 with $n = 1$, when Y is a hydroxyl, and x has a sufficient value to confer on the oils of formula (1) a dynamic viscosity at 25°C of between 1 000 and 200 000 mPa.s,

this C POS being intended to react with another C POS or with at least one crosslinking agent D,

- and/or at least one nonreactive E POS

different from the C POS(s);
and in that the following are incorporated:

- o a catalytic system comprising a
condensation metal catalyst;
- 5 o optionally one or more semireinforcing,
nonreinforcing or bulking fillers;
- o optionally water;
- o optionally one or more additives chosen
from pigments, plasticizers, other rheology
10 modifiers, stabilizers and/or adhesion
promoters.

15. Method according to any one of Claims 1
to 10, characterized in that a polydehydrogeno-
condensation SM SM₃ is used which contains:

- 15 ▪ at least one C' type POS carrying hydroxyl
crosslinking functional groups Fc' and/or
OR' functional groups (R' = C₁-C₃₀ alkyl,
C₂-C₃₀ alkenyl, aryl, optionally substituted
(preferably halogenated)) precursor of the
20 functional groups Fc', these crosslinking
functional groups Fc' being capable of
reacting with other crosslinking functional
groups Fb' (SiH) of at least one B' type
POS, this C' POS being taken alone or as a
25 mixture with at least one nonreactive (E)
POS;
- at least one reactive silicone oil B' POS,

whose crosslinking functional groups, Fb',
are hydrogen functional groups, this B' POS
comprising at least two $\equiv\text{Si-H}$ groups per
molecule (preferably at least three when
the A POS comprises only two $\equiv\text{Si-Vi}$ groups
per molecule), these $\equiv\text{Si-H}$ groups being
advantageously present in the chain;

- and/or at least one nonreactive E POS;

and in that the following are incorporated:

- o a catalytic system comprising a
polydehydrogenocondensation metal catalyst
(preferably of platinum nature) and
optionally an inhibitor;
- o optionally one or more semireinforcing,
nonreinforcing or bulking fillers;
- o optionally water;
- o optionally one or more additives chosen
from pigments, plasticizers, other rheology
modifiers, stabilizers and/or adhesion
promoters.